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1,102,921



## PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

## Stabilised polyamide compositions.

- We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:
- This invention relates to synthetic linear fibre forming polyamides having improved resistance to oxygen at elevated temperatures and also to synthetic linear fibre-forming polyamides having improved resistance to light.
- It is known that synthetic linear fibre forming polyamides such as polyhexamethylene adipamide and polycaprolactam tend to be discoloured by exposure to hot air, as for example during the heat setting of nylon fabric. We have now found that polyamides with good resistance to degradation by hot air can be obtained when tungsten or molybdenum are present in the form of their chemical compounds.
- According to the present invention we provide synthetic linear fibre forming polyamides containing an inorganic oxy-compound of tungsten or an inorganic oxy-acid of molybdenum.
- The tungsten may be added, for example, as tungstic acid or a polytungstic acid, or as a tungstate or polytungstate, for example sodium tungstate, ammonium metatungstate, or hexamethylene diamine tungstate, as tungsten trioxide, or as a heteropolytungstic acid, for example a silicotungstic acid, phosphotungstic acid (especially dodecatungstophosphoric acid), or phosphomolybdotungstic acid, or as a phosphotungstate such as sodium phosphotungstate or ammonium phosphotungstate.
- The molybdenum may be added, for example, as molybdic acid or a polymolybdic acid, or a molybdate or polymolybdate, for example ammonium molybdate, or as a heteropolymolybdic acid (or salt thereof), for example a silicomolybdic acid, phosphomolybdic acid or phosphomolybdotungstic acid.
- Preferably the tungsten or molybdenum is present in the proportion of from 0.001% to 1.0% by weight calculated as the metal.
- The tungsten or molybdenum may be added to the polyamides if desired together with materials already known to improve light or heat stability, for example manganese compounds or copper compounds optionally together with phosphate or halide salts. Especially suitable materials of this kind containing manganese compounds are those further described in U.K. Patent Specifications Nos. 861,354 and 862,577 and in our co-pending Application No. 33683/62 (U.K. Specification No. 997,316), for example polyphosphate complexes produced by reacting a manganese salt with an alkali metal polyphosphate or an alkali metal polymetaphosphate, or a phosphate of divalent manganese or a non-complex double phosphate of divalent manganese and ammonia and/or an alkali metal, or mixtures of a manganese compound with an oxy compound of phosphorus (for example an ortho or pyrophosphate salt). Suitable materials containing copper and halide or other compounds are described for example in U.K. Patent Specification No. 722,724, (U.S. Patent Specification No. 2,705,227) and U.K. Patent Specification No. 839,067, (U.S. Patent Specification No. 2,960,489), for example a copper compound (for example copper acetate) and an alkali metal or ammonium halide (for example sodium iodide) or a copper compound and the halide of an organic base. Very small amounts of copper and halide compounds are sometimes found to be effective, for example from 3 to 9 parts per million of a copper compound (calculated as Cu) may be added together with from 100 to 900 parts per million of an

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alkali metal, ammonium or organic base hydrogen halide, by weight of the polyamide.

It is also known that synthetic linear fibre forming polyamides such as polyhexamethylene adipamide and polycaprolactam tend to be degraded by exposure to light, especially when they contain pigments such as titanium dioxide which are often employed to increase the opacity of fibres made from these polyamides, and it has been proposed to improve the light stability of pigmented polyamides by incorporating manganese compounds in the polyamides. However, the manganese compounds which have been used hitherto have usually had the disadvantage of being affected by certain bleaching agents, and this has led to discolouration difficulties in the processing of textile materials made from polyamides containing these manganese compounds. We have now found that pigmented polyamides with good resistance to degradation by light and improved properties in respect of susceptibility to discolouration by bleaching agents such as alkali metal chlorites can be obtained when there is present in addition to manganese either tungsten or molybdenum in the form of their chemical compounds.

Thus according to a further feature of the present invention we provide synthetic linear fibre forming polyamides containing a pigment and manganese and either tungsten or molybdenum, the manganese and the tungsten or molybdenum being present in the form of one of their chemical compounds.

Preferably the manganese is present as a manganese tungstate or phosphotungstate or as a manganese molybdate or phosphomolybdate or as a chemical equivalent of these compounds. Thus the manganese may be added to the polyamide during or after manufacture of the polyamide in combination with some other radical than the tungstate, phosphotungstate, molybdate or phosphomolybdate radical for example, as manganese acetate, oxalate, adipate, lactate, orthophosphate, pyrophosphate or any of the manganese compounds known from the art to improve the light stability of pigmented synthetic linear fibre forming polyamide. The tungsten or molybdenum may be added in the form of any of the compounds of tungsten or molybdenum, for example those compounds which have already been mentioned. Such additions of manganese and tungsten or molybdenum compounds are to be regarded as equivalent to additions of manganese tungstate or phosphotungstate or manganese molybdate or phosphomolybdate for the purpose of the present invention.

Preferably the manganese is employed in the proportion of from 5 parts per million to 100 parts per million by weight of the polyamide (calculated as manganese), and the tungsten or molybdenum is present

preferably in the proportion of from 0.001% to 0.25% (10 to 2500 parts per million) by weight calculated as tungsten or molybdenum.

Usually the manganese and tungsten or molybdenum are employed in amounts relative to each other such that the metals are present approximately in the ratio of their atomic weights, but different proportions can be used if desired.

The pigment, for example titanium dioxide, is normally present in an amount within the range 0.02% to 3.0% by weight of the polyamide.

When improved heat resistance as well as improved light resistance is required it is found that additions of copper compounds and halide compounds can be made together with the additions of combined manganese and combined tungsten or molybdenum, and such mixed additives are found to have only a small effect on the state of the dispersion of the delustrant in the polyamide. Suitable copper and halide compounds are those already mentioned.

The tungsten or molybdenum and other additions are preferably made during the manufacture of the polyamides, that is the additions are made to the polyamide forming components during polymerisation, or the additions may be made after polymerisation or during conversion of the polyamide to fibres.

The invention is illustrated by the following Examples in which the parts and percentages are by weight:

#### Example 1

A mixture of 262 parts of hexamethylene diammonium adipate, 175 parts of water, 0.6 parts of acetic acid, and 0.42 parts of dodecatungstophosphoric acid was heated in an autoclave in the absence of air. When, at a temperature of about 215°C., the pressure had risen to 250 p.s.i.g. it was maintained at this level by releasing steam. About ten minutes after the start of steam release 4.52 parts of  $TiO_2$  dispersed in water was added to the autoclave and heating was continued until the temperature had risen to 245°C. The pressure was then gradually reduced to atmospheric pressure 90 minutes while heating was continued so that the temperature rose to 270°C. Polymerisation was continued at 270-275°C. and atmospheric pressure for a further 30 minutes and the polymer was then extruded from the autoclave under nitrogen pressure, quenched in water and cut into small flakes. The polymer was then melt spun and drawn in conventional manner to continuous filaments.

A composite warp-knitted fabric was then prepared having a broad stripe of the nylon filaments prepared as described above, lying between "control" stripes of nylon filaments

prepared in a similar manner but omitting the dodecatungstophosphoric acid. The composite fabric was then heat set on a stenter at 230°C. for 30 seconds. After this treatment the stripe containing tungstophosphoric acid modified polymer remained white, whereas the unmodified fabric had turned yellow.

#### Example 2

A mixture of 262 parts of hexamethylene diammonium adipate, 175 parts of water, 0.6 parts of acetic acid and, 0.5 parts of manganous acetate tetrahydrate, 0.42 parts of dodecatungstophosphoric acid, 0.0035 parts of cupric acetate monohydrate, and 0.1 parts of hexamethylene diammonium iodide was polymerised by the process described in Example 1. The polymer was converted into continuous filament yarn by conventional methods and the yarn was introduced into a warp-knitted fabric as a broad stripe bounded by standard 66 nylon yarns. After heat setting at 230°/30 seconds the fabric generally had a yellow colouration except in the stripe of fabric containing tungstophosphoric acid, which remained white.

#### Example 3

A mixture of 262 parts of hexamethylene diammonium adipate, 175 parts of water, 0.6 parts of acetic acid, 0.05 parts of manganous acetate tetrahydrate and 0.42 parts of dodecatungstophosphoric acid was heated in an autoclave in the absence of air. When, at a temperature of about 215°C, the pressure had risen to 250 p.s.i.g. it was maintained at this level by releasing steam. About ten minutes after the start of steam release 4.52 parts of  $TiO_2$  dispersed in water was added to the autoclave and heating was continued until the temperature had risen to 245°C. The pressure was then gradually reduced to atmospheric pressure over 90 minutes while heating was continued so that the temperature rose to 270°C. Polymerisation was continued at 270-275°C. and atmospheric pressure for a further 30 minutes and the polymer was then extruded from the autoclave under nitrogen pressure, quenched in water and cut into small flakes. The resultant white polymer was not discoloured after treatment with sodium chlorite solution, whereas a similar polymer from which the tungstophosphoric acid had been omitted was stained brown under the same conditions.

#### Example 4

A mixture of 262 parts of hexamethylene diammonium adipate, 175 parts of water, 0.6 parts of acetic acid, 0.05 parts of manganese acetate tetrahydrate and 0.05 parts of sodium molybdate dihydrate was heated in an autoclave in the absence of air. When, at a tem-

perature of about 215°C., the pressure had risen to 250 p.s.i.g. it was maintained at this level by releasing steam. About ten minutes after the start of steam release 4.52 parts of  $TiO_2$  dispersed in water was added to the autoclave and heating was continued until the temperature had risen to 245°C. The pressure was then gradually reduced to atmospheric pressure over 90 minutes while heating was continued at 270-275°C., and atmospheric pressure for a further 30 minutes and the polymer was then extruded from the autoclave under nitrogen pressure, quenched in water and cut into small flakes.

The resultant polymer was not discoloured after treatment with sodium chlorite solution, whereas a similar polymer from which the sodium molybdate had been omitted was stained brown under the same conditions.

#### WHAT WE CLAIM IS:—

1. Synthetic linear fibre forming polyamides containing an inorganic oxy-compound of tungsten or an inorganic oxy-acid of molybdenum.
2. Polyamides as claimed in claim 1 wherein the tungsten compound is added as tungstic acid or a polytungstic acid, as a tungstate or polytungstate, as tungsten trioxide, as a heteropolytungstic acid or as a phosphotungstate.
3. Polyamides as claimed in either of claims 1 or 2 wherein the tungsten compound is added as a phosphotungstic acid.
4. Polyamides as claimed in any one of the preceding claims wherein the molybdenum compound is added as molybdic acid or a polymolybdic acid, as a molybdate or polymolybdate or as a heteropolymolybdic acid or salt thereof.
5. Polyamides as claimed in any one of the preceding claims wherein the tungsten compound or molybdenum compound is present in the proportion of from 0.001% to 1.0% by weight calculated as the metal.
6. Polyamides as claimed in any one of the preceding claims and which also contain manganese compounds.
7. Polyamides as claimed in any one of the preceding claims and which also contain copper compounds.
8. Polyamides as claimed in claim 7 and which also contain halide salts.
9. Polyamides as claimed in claim 8 wherein the halide salt is an alkali metal or ammonium halide or the hydrogen halide of an organic base.
10. Polyamides as claimed in any one of claims 6 to 9 and which also contain a pigment.
11. Polyamides as claimed in claim 10 wherein the manganese compound is present as manganese tungstate or phosphotungstate or as a manganese molybdate or phosphomolybdate.

12. Polyamides as claimed in either of claims 10 or 11 wherein the manganese is added in combination with some other radical than the tungstate, phosphotungstate, molybdate or phosphomolybdate radical.
13. Polyamides as claimed in any one of claims 10 to 12 wherein the manganese is added as manganese acetate, oxalate, adipate, lactate, orthophosphate or pyrophosphate.
14. Polyamides as claimed in any one of claims 10 to 13 wherein the manganese compound is present in the proportion of from 5 parts per million to 100 parts per million by weight of the polyamide calculated as manganese.
15. Polyamides as claimed in any one of claims 10 to 14 wherein the tungsten or molybdenum compound is present in the proportion of from 0.001% to 0.25% by weight of the polyamide calculated as tungsten or molybdenum.
16. Polyamides as claimed in any of claims 10 to 15 wherein the manganese and tungsten compounds are present in amounts relative to each other such that the metals are present approximately in the ratio of their atomic weights.
17. Polyamides as claimed in any of claims 10 to 16 wherein the manganese and molybdenum compounds are present in amounts relative to each other such that the metals are present approximately in the ratio of their atomic weights.
18. Polyamides as claimed in any one of claims 10 to 17 in which the pigment is titanium dioxide.
19. Polyamides as claimed in any one of the preceding claims in which the polyamide is polyhexamethylene adipamide.
20. Polyamides as claimed in claim 1 substantially as described in any one of the Examples.
21. Polyamides as claimed in claim 10 substantially as described in either of Examples 3 or 4.
22. A process for the manufacture of the polyamides claimed in any one of the preceding claims which comprises adding an inorganic oxy-compound of tungsten or an inorganic oxy-acid of molybdenum to the polyamide forming components during polymerisation and completing the polymerisation.
23. A process for the manufacture of the polyamides claimed in any of claims 10 to 18 or 21 which comprises adding a pigment, a manganese compound, and either an inorganic oxy-compound of tungsten or an inorganic oxy-acid of molybdenum to the polyamide forming components during polymerisation and completing the polymerisation.
24. A process for the manufacture of synthetic linear fibre forming polyamides containing an inorganic oxy-compound of tungsten or an inorganic oxy-acid of molybdenum substantially as described in any one of the Examples.

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